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Résumé - Les contacts redresseurs N^+ de photopiles au silicium polycristallin (Wacker, HEM, CGE) ont été réalisés soit par implantation conventionnelle du dopant (P^+) soit par "incrustation" d'ions (implantation sans séparation magnétique PF_5). Deux techniques de recuit de surface par faisceau laser en phase liquide (laser Nd : YAG) et en phase solide (laser CO_2) ont été employées. Les performances des photopiles ainsi élaborées ont été étudiées. Pour les deux types de dopage et de recuit, le rendement de conversion photovoltaïque des cellules dépasse 11% AM1 pour les matériaux polycristallins utilisés.

Abstract - Conventional ion implantation and unanalyzed ion bombardment have been used to elaborate the rectifying N^+ contact of polycrystalline silicon (Wacker, HEM, CGE) solar cells. Two surface laser annealing in the liquid phase (Nd : YAG laser) and in the solid phase (CO_2 laser) regimes have been used. The properties of the solar cells so processed have been investigated. For both doping procedures and both annealing techniques, the cells (conversion) efficiencies under AM1 illumination exceeded 11% for the various polysilicon substrates.

I - INTRODUCTION

Laser annealing techniques, associated with ion implantation are considered as possible ways of reducing the cells production cost. Furthermore, a cold process may become particularly attractive in the case of polysilicon, because the doping thus achieved may become independent on the crystalline orientation of each crystal. In addition, the laser annealing, pulsed or scanned, prevents any preferential diffusion at the grain boundaries.

In this study two laser annealing procedures have been investigated in order to activate the implanted dopant, namely a pulsed YAG laser operating in the liquid phase regime and a continuous CO_2 laser working in the solid phase regime. At 0.53 micron wavelength, the absorption is essentially due to band to band transitions, whereas at 10.6 micron the free carrier absorption is by fare dominant, so that a moderate heating of the substrate is necessary to initiate the coupling.

The experiments have been performed on various types of polycristalline silicon (Wacker, HEM and polysilicon under evaluation at Laboratoires de Marcoussis - CGE) doped by two implantation procedures : classical ion implantation of phosphorus and non-mass analysed molecular ions bombardment of PFn (n = 0 to 5) by using the procedure already described called ion "incrustation" (1).

II - LASER ANNEALING

1. Pulsed laser processing (liquide phase epitaxy) :

PHASE Laboratory is equiped with a Nd : YAG laser (mounted with a frequency doubler λ = 0.53 micron) from QUANTRONIX. The characteristics of the laser are the following : pulse duration 100 nsec, spot diameter adjustable from 70 to 170 microns to obtain energy densities from 0.5 to 3 J/cm^2 for repetition rates ranging from 3 to 10 KHz. The main problem of this kind of laser processing is to find an adequate spot overlapping rate so that the whole silicon surface is annealed with an energy density about twice the threshold energy allowing the melting of the surface. The melting of the front amorphized layer has a duration of some hundred nsec (2) and is immediately followed by a fast epitaxial regrowth in the liquid phase regime, incorporating a very high concentration of dopant into substitutional sites. Figure 1 shows the principle of the high speed motion system which uses a microprocessor set up to control the rotation of the target disc and the displacement of the radial arm bearing the focusing system of the beam. The experimental optimum throughout determined for the tests reported hereunder is of six 4 inch wafers per hour.

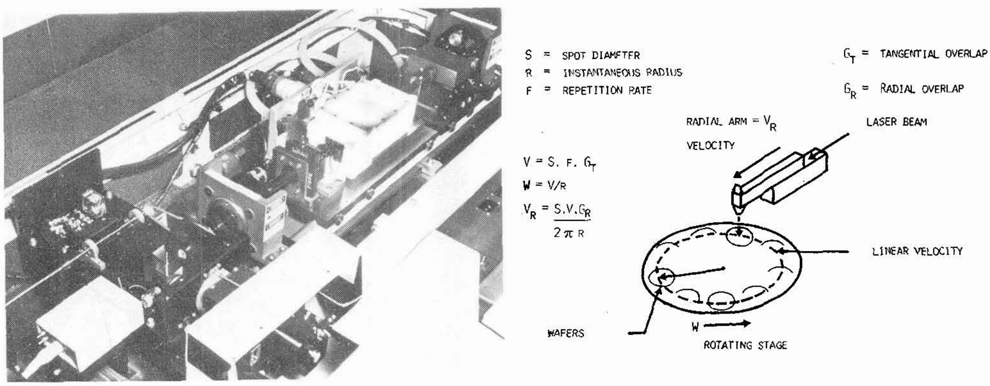

Fig 1 : Nd : YAG laser system : general view and schematic of the high speed motion system.

2. Continuous CO_2 laser processing (solid phase epitaxy)

As reported hereupon at a 10.6 µm radiation a moderate heating or a simultaneous illumination by photons of a convenient wavelength is necessary to enhance the absorption. The photon energy is absorbed by free-carriers in either conduction or valence band and the free-carriers with a small contribution due to multiphonon excitations directly transform the absorbed energy into heat [3] . In these conditions the regrowth occurs via solid phase epitaxy and without any melting [4] .

Treatments were performed by Laboratoires de Marcoussis at a 10.6 µm wavelength with a CW CO_2 laser capable of delivering up to 30 W (multimode) output in an approximately Gaussian beam. The beam was focused by a germanium lens of 100 mm focal length on a wafer holder which could be heated up to 500°C. The power density in the range from 1 to 9 kW/cm^2 was controlled by moving the focusing lens in respect with the sample holder. The displacements under the beam were achieved by X, Y movements. In the X direction the speed was 6 cm/mn and the displacements in the perpendicular direction could be adjusted at the desired step in order to obtain variable overlapping rates. Figure 2 shows a general view of the CO_2 laser system and its schematic.

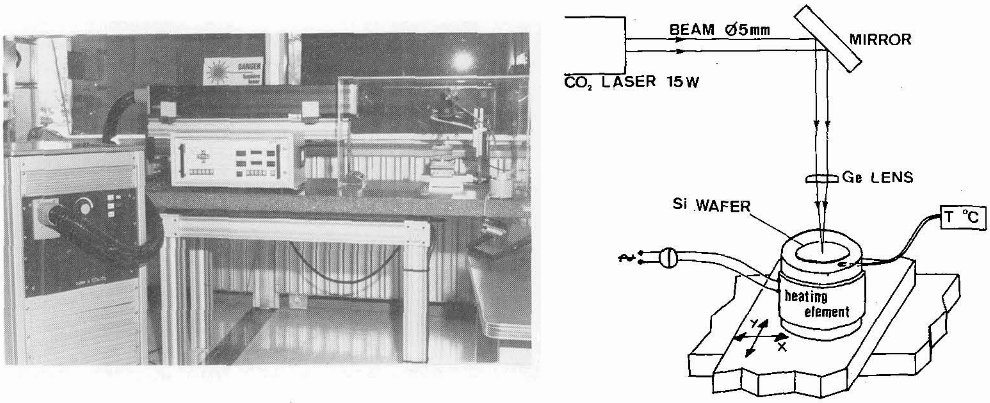

Fig 2 : CW CO_2 laser system.

The influence of various parameters such as the power density, the temperature of the substrates and the overlapping rate was earlier reported [5] . The results (sheet resistance, local photoresponse) have shown i) for power densities lower than 4 kW/cm^2 a solid phase recrystallization takes place on the whole width ii) at 450°C with typical annealing conditions (2,2 kW/cm^2 ; step - 0,5 mm) a sheet resistance less than 100 $\Omega/\square$ is achieved in the case of a phosphorus implantation iii) a low overlapping rate is sufficient to obtain an homogeneous annealing in the whole silicon surface.

III - APPLICATION TO SOLAR CELLS

1. Fabrication process :

The fabrication process of the cells included the following steps :

- material : P type polysilicon of resistivity about 1 Ω.cm, from Wacker, HEM and CGE have been processed after surface acid preparation,
- doping : implantation of $^{31}P^+$ at 20 keV at a dose of 5.10^{15} ions/cm^2 and non-analyzed molecular and atomic PF_5 at 10 keV for doses between 1 and 5.10^{16} ions/cm^2.
- two laser processes have been used for annealing :
  - the YAG laser focused on pulses of 100 microns in diameter with an energy of 2.5 J/cm^2. The repetition rate was 5 KHz and the following overlapping conditions were adopted : SG_T and SG_R = 20 microns with a disc velocity of 10 cm/s.
  - the continuous CO_2 laser operating at a power of 15 W. The beam, 5 mm in diameter was focused to a spot of 0.7 mm on the wafer holder heated up to 450°C.
- contacts manufacturing : the metallization of the back contact was obtained by evaporation of a triple layer of Ti-Pd-Ag and was followed by a sintering at 600°C during 20 minutes. This sintering was also used as a post laser thermal treatment in the case of the pulsed process. The same evaporation process was used to metallize the grid on the front face and was followed by the deposition of a N_4Si_3 antireflective coating.

The cells total area was typically 11 cm^2 corresponding to an active area of 10 cm^2.

2. Solar cells performances :

The characteristics of the cells so elaborated were investigated by using sheet resistance, dark current and under AM1 illumination measurements. Tables I and II give the photovoltaic performances of the cells doped respectively by PF_5 ion incrustation and P^+ ion implantation. Former results obtained on monocrystalline silicon cells are given for comparison [6] .

In the case of PF_5 doping, table I shows that open circuit voltages Voc between 540 and 570 mV are obtained after a pulsed annealing for the various polycristalline materials. Concerning the CO_2 laser annealing, the first results achieved for not yet optimized doping conditions indicate lower values of Voc. It is now established that a higher doping energy than those reported on table I is required in the case of a solid phase epitaxial regrowth which produces no significant redistribution of the dopant [7] . It must be noted that Voc values as high as 585 mV have been achieved on monocrystalline solar cells. On the contrary, the short circuit current density values (Jsc) obtained in the case of the CO_2 laser annealing are higher than those measured on pulsed-annealed cells. This difference probably results from a more superficial junction with a lower level of residual defects in the charge space region. AM1 efficiencies in excess of 10% were achieved with the various polycristalline materials. For example, a 12% output was measured on HEM silicon.

Table II gives similar results obtained on P^+ doped cells. The following points can be noted i) slightly better performances were achieved on cells annealed with the CO_2 laser and ii) the two annealing processes give not so different values of Voc as in the case of a PF_5 doping. Efficiencies between 10 and 12% AM1 were also measured on the P^+ doped various polycristalline materials.

Silicon materials	Laser annealing	Voc (mV)	Jsc (mA/cm^2)	FF	η % (AM1)
Single crystal	YAG - 2.5 J/cm^2	585	32.6	0.7	13.3
	CO_2 - 1.8 kW/cm^2	523	33.4	0.64	11.2
SILSO	YAG - 2.5 J/cm^2	539	27.8	0.71	10.6
HEM	YAG - 2.5 J/cm^2	542	30.8	0.72	12
CGE	YAG - 2.5 J/cm^2	567	29.2	0.63	10.4
(not optimized)	CO_2 - 3 kW/cm^2	510	33.9	0.6	10.3

Table I : PF_5 implantation.

Silicon materials	Laser annealing	Voc (mV)	Jsc (mA/cm^2)	FF	η % (AM1)
Single crystal	YAG - 2.5 J/cm^2	575	32.6	0.7	13.1
	CO_2 - 1.5 kW/cm^2	553	33.3	0.71	13
SILSO	CO_2 - 3 kW/cm^2	537	32.5	0.69	12
HEM	YAG - 2.5 J/cm^2	554	26	0.72	10.4
	CO_2 - 3 kW/cm^2	538	25.7	0.74	10.2
CGE	YAG - 2.5 J/cm^2	555	31.3	0.65	11.3
(not optimized)	CO_2 - 3 kW/cm^2	537	32.4	0.67	11.6

Table II : P^+ implantation.

IV - DISCUSSION AND CONCLUSION

The first point that emerges from this study concerns the non mass analyzed implantation technique : the results indicate that this process gives photovoltaic junctions so performant as those elaborated by ion implantation with mass-analysis. This is an interesting point since "incrustation" has significant advantages by comparison with classical processes.(lower cost of machine, less onerous maintenance requirements).

The second point relates to the laser processing techniques. Comparison of Tables I and II indicates that the pulsed annealing gives better performances and more especially better Voc values than a continuous annealing. The difference must be related to the fact that the liquid phase epitaxial regrowth of the YAG laser brings about a better activation of the dopant and a more perfect recovery of the amorphized zone. In the case of a solid phase regrowth induced by the CO_2 laser, a Rutherford Backscattering analysis of $^{75}As^+$ implanted <111> silicon annealed at an energy between 2 and 4 kW/cm^2 showed that only 34% of As is on substitutional position and that residual defects subsist in the doped layer (X_{min} Si ≃ 10%). A more sensitive technique (DLTS) shows that deeper in the crystal, in the charge space region of the junction, residual point defects subsist in the zone not reached by the melt front in the case of the liquid phase process [8] . This kind of measurement must be done for a CO_2 laser process to confirm that solid phase regrowth is more suitable to anneal deep lying residual defects [9] .

These two points : lack of activity of the dopant and poor recrystallization of the front layer can probably be improved by using more energetic laser beams with of course higher processing throughput rates. Calculations have shown that rates of several m^2/h could be reached which would be compatible with the doping rates of multiple beams ion source presently developped [10] . Concerning pulsed annealing it must be pointed out that UV gas Excimer Lasers have been recently used to produce very efficient implanted junctions for solar cells [11] . Moreover the pulse shape (flat profile) and the beam large section will probably meet large production rates. So these two laser systems (EXCIMER and CO_2) must be regarded as a possible mean of achieving significant reductions in solar cells costs.

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